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## ADVANCED SUPERCRITICAL FUELS

AFOSR Task # 93WL002

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### SUMMARY/OVERVIEW:

Increases in aircraft and engine performance are increasing the heat load being transferred into an aircraft's primary coolant--the fuel. This research is aimed at understanding the limitations of operation of fuel heated to 480 C (900 F) and beyond. Important issues are expected to be thermal stability, heat transfer/flow instabilities, and injection/combustion properties.

### TECHNICAL DISCUSSION

Jet fuels are almost intractably complex, containing hundreds of hydrocarbons in an ever-shifting mix driven by source crude oil composition and processing. One approach for modeling and experimentation is the use of "surrogates"--simpler mixtures of hydrocarbons to represent the properties of interest. The complexity of the surrogate required varies with the fuel property being studied [1]. Another approach is to use multivariate analysis techniques on the principal fuel components (as determined by gas chromatography) to create eigenvalues and eigenvectors characteristic of each fuel. As shown in Figure 1, multiple analyses of single samples of JP-5, 7, and 8 show that the reproducibility from GC trace to GC trace is sufficient to identify differences between the various fuels. This time-intensive and tedious approach is being extended to multiple samples of each fuel. JP-8's (and Jet A's) can vary widely and it remains to be seen if the natural variation among samples will still allow the fuel types to be identified using this technique. The study of the properties of supercritical fuels continues, with the study of supercritical injection behavior [13] and with an analysis of the effect of hydrocarbon type on solvent-solute interactions. As shown in Figure 2, fluorescence of pyrene is being used to probe the effects of pressure (density) on solvent/solute interactions [9,15]. The differences between the hydrocarbons shown was the initial observation of such a structural effect and was unexpected.

Studies of thermal-oxidative and pyrolytic deposition continue [4,5,10,11,14,16]. A surprisingly strong interaction between deposition and the character of the fuel-wetted surface has been identified. As shown in Figure 3, several tests were performed with a silica-coated tube (Silcosteel®) of various lengths, joined to a stainless steel tube. In a series of tests, the silcosteel/stainless junction was moved to various locations along the heated zone, representing different portions of the fuel oxidation pathway. Early in the fuel oxidation process, the character of the heated surface appears to be relatively unimportant. But, as the junction is moved past the point of maximum deposition, a dramatic decrease in deposition is seen. This indicates the surface is active in the deposition process, as opposed to the early oxidation

processes that lead to deposition. In combination with the use of the dispersant additive in JP-8+100, the deposition is reduced by almost two orders of magnitude with the use of Silcosteel. It is expected that achievement of high thermal stability required by advanced applications [2,3,8,12] will require a combination of advanced additives, fuel deoxygenation, and an inert surface coating like Silcosteel. Pyrolytic deposition is important at 900 F (480 C) and above, and is also being studied [10,11,14]. The complexities of jet fuel pyrolysis are almost overwhelming, with the stability ranking of fuels changing as a function of fuel time-temperature-pressure history. In general, it appears that the formation of aromatics inside the fuel system is a precursor to pyrolytic deposit formation, analogous to PAH formation being a precursor to soot formation. An initial analysis has attempted to link both processes in a time-scale analysis [7].

New diagnostic approaches are being examined to probe the complex processes occurring as jet fuels are heated. The ultimate goal of this work is a field- or flight-portable instrument that can rapidly assess the state of the fuel, as opposed to the spectrum of time-consuming and costly tests used now to assure jet fuel quality and to study its reactions. One option being examined is the "chemical nose", which has the potential to identify fuels and reactions pathways with a group of 32 sensors sensitive to various hydrocarbons.

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13. Ervin, J. S., Williams, T. F., Bento, J., Doungthip, T., "Studies of Jet Fuel Thermal Stability and Flow Characteristics within a Nozzle Under Supercritical Conditions," *ACS Petroleum Chemistry Division Preprints*, Volume 45(3), pp. 538-541, August 2000.

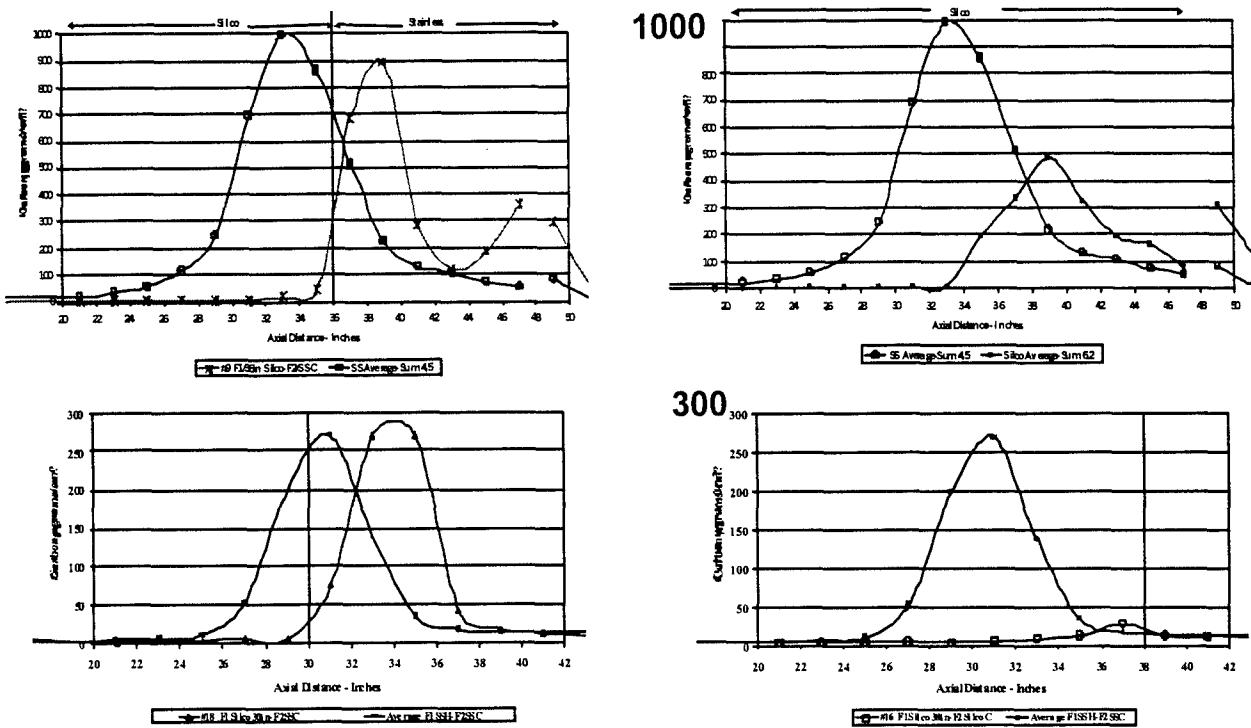


Figure 3 – (top left and right) Deposition profiles in tests with varying tube surfaces. (top left) deposition peak at roughly 1000 for stainless steel, deposition peak shifted to right and lowered by tube transitioning from stainless to Silcosteel at vertical line. (top right) Deposition profile for totally-Silcosteel-lined tube (lower profile), compared with stainless steel. (lower left) JP-8+100 deposition profile in stainless steel (left peak) compared with stainless steel/silcosteel tube[change at line]. (lower right) Deposition profile for primarily Silcosteel tube (low curve) as compared to original JP-8+100/stainless steel deposition curve.

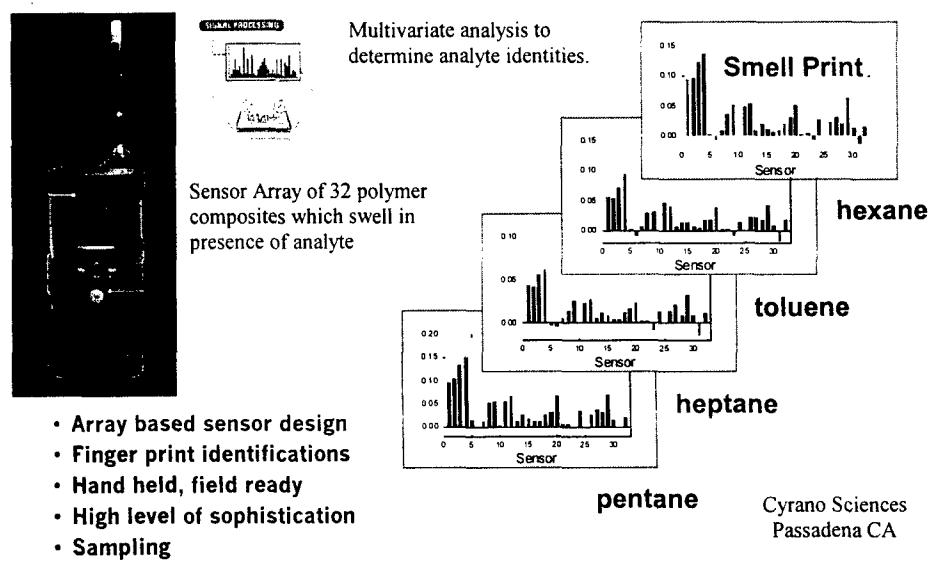


Figure 4 – Chemical nose concept.

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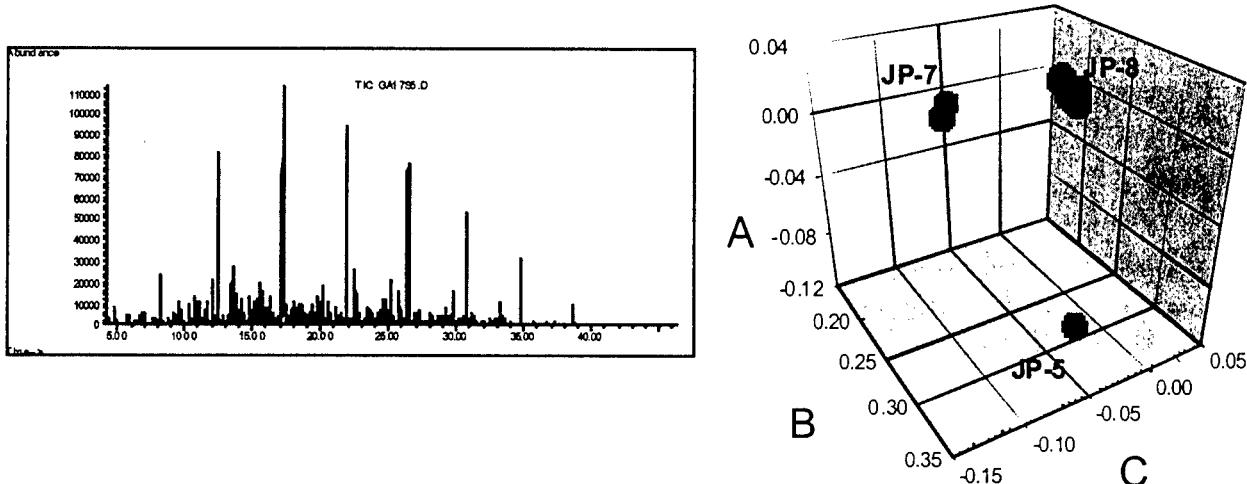


Figure 1 – Multivariate analysis of GC/MS data shows measurable differences between JP fuels.

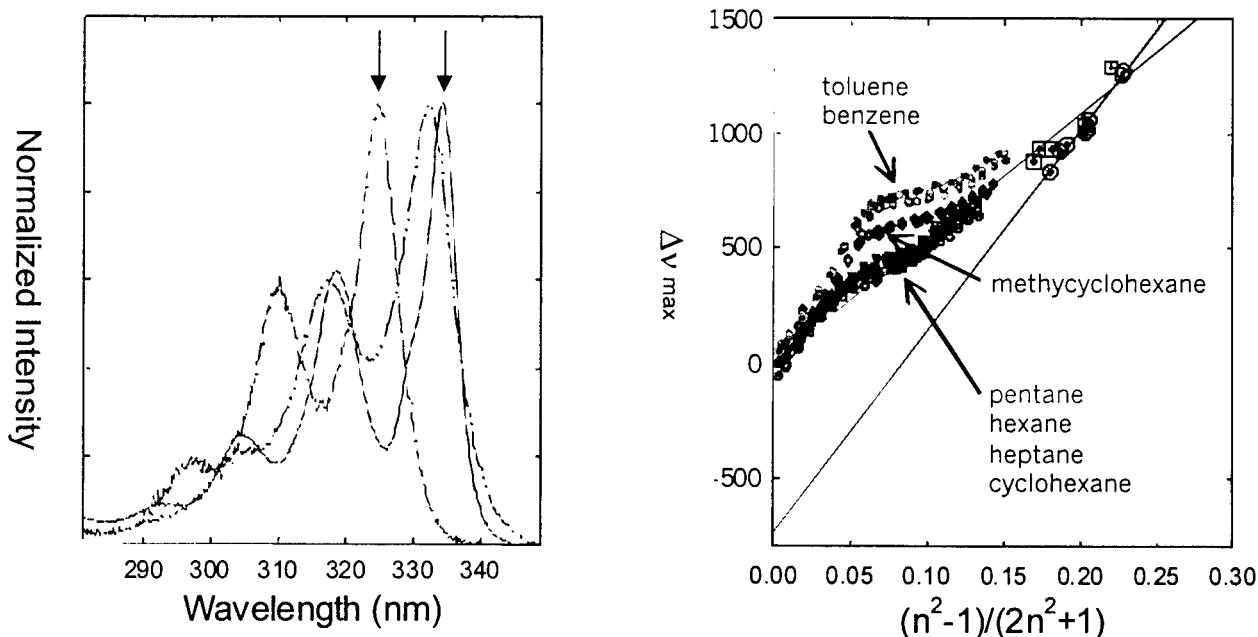


Figure 2 – (left) Pyrene fluorescence spectra in supercritical hexane at 245 C at various pressures; (right) shift in peak of fluorescence as a function of dispersion parameter (pressure).